Preparation of Carbodiimides by the Reaction of Dimetallothioureas with Sulfur Dioxide

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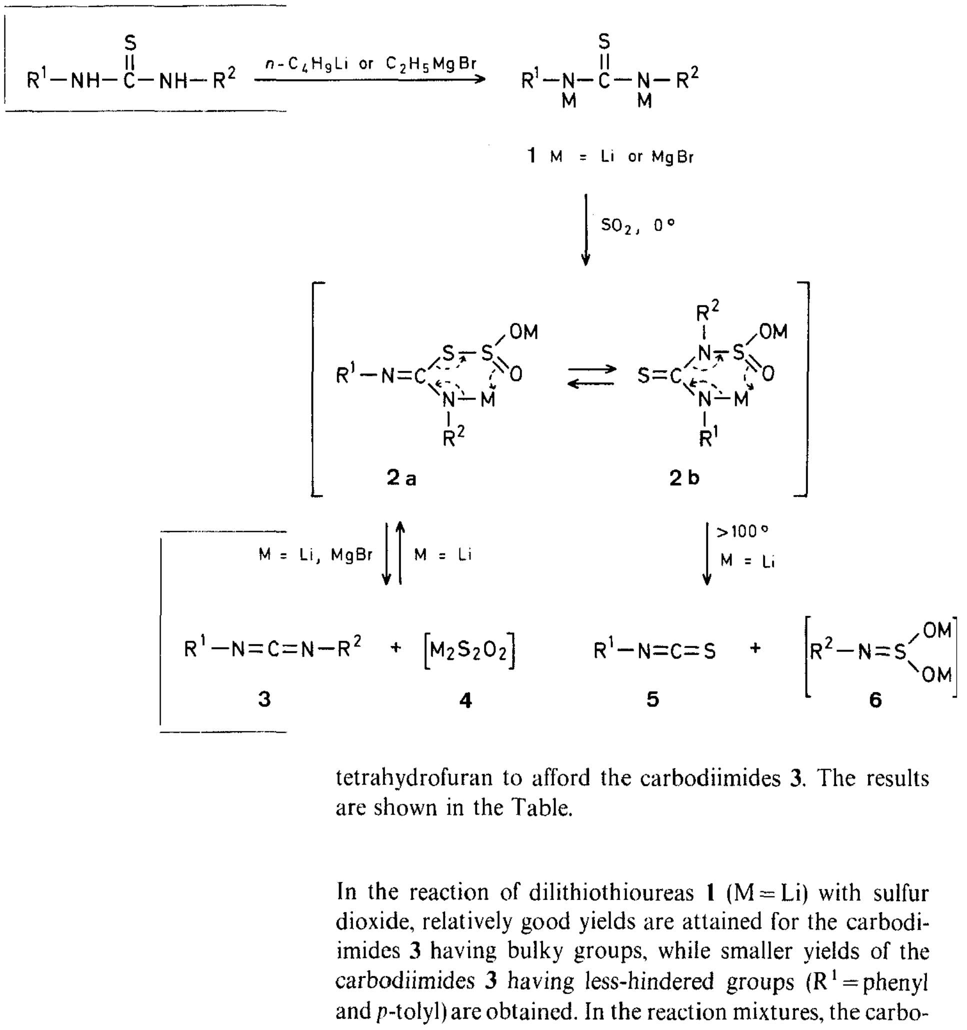
The usual methods for the synthesis of carbodiimides involve the use of poisonous reagents such as mercury(II) salts[1], or phosgene derivatives[2].

We have recently reported on the transformations of dilithio- or bis[bromomagnesio]-thioureas **1** to the corresponding carbodiimides **3** by thermal decomposition at 170–200°, or by reaction with carbon disulfide below room temperature[3]. However this procedure is not applicable to the preparation of the carbodiimides **3** having sterically less-hindered substituents such as phenyl and *p*-tolyl groups. Futhermore, in the case of the reaction of the dilithiothioureas **1** (M = Li) with carbon disulfide, a rapid separation of the products is essential because the carbodiimides **3** formed reversibly react with the by-product Li_2CS_3 to afford the corresponding isothiocyanates **5**[4].

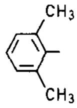
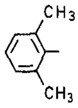
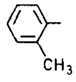
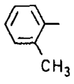
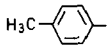
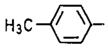
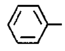
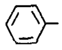
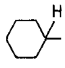
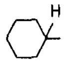
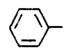
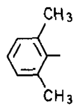
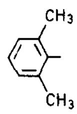
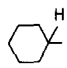
We report here an alternative method for the preparation of the carbodiimides **3** using dimetallothioureas and sulfur dioxide, in which case the reverse reaction to form the isothiocyanates **5** scarcely occurs. Dimetallothioureas **1**, prepared *in situ* from thioureas and two equivalents of butyllithium or ethylmagnesium bromide, react with sulfur dioxide in tetrahydrofuran to afford the carbodiimides **3**. The results are shown in the Table.



In the reaction of dilithiothioureas **1** (M = Li) with sulfur dioxide, relatively good yields are attained for the carbodiimides **3** having bulky groups, while smaller yields of the carbodiimides **3** having less-hindered groups (R^1 = phenyl and *p*-tolyl) are obtained. In the reaction mixtures, the carbodiimides **3** are stable in refluxing tetrahydrofuran, but are converted to the corresponding isothiocyanates **5** by heating above 100° in the absence of a solvent.

Contrary to the reaction of dilithiothioureas **1** (M = Li), that of bis[bromomagnesio]thioureas **1** (M = MgBr) with sulfur dioxide is a more useful synthetic method for the carbodiimides **3**, since there is no limitation to the kind of substituents in compound **1** or **3**, and the carbodiimides **3** are stable in the reaction mixture even at 100°. These advantages may be due to the low reactivity of the eliminated salt **4** (M = MgBr; not able to be isolated for identification as yet) toward the carbodiimides **3**.

Table. Carbodiimides 3 from Dimetallothioureas 1 and Sulfur Dioxide

R¹	R²	Yield [%] M = Li[a], MgBr[b]	b.p./torr (Lit. b.p./torr)	I.R. (neat) $\nu_{N=C=N}$
		52, 71	148–152°/0.7 (122–123°/0.5)[5]	2180 cm⁻¹
		80, 55	125–130°/0.5 (118–122°/0.1)[2]	2145 cm⁻¹
		15, 54	140–141°/0.8 (165°/2.4)[2]	2120 cm⁻¹
		trace, 49	131–135°/2.0 (119–121°/0.5)[2]	2120 cm⁻¹
		67[c], 47	101–103°/0.6 (98–100°/0.5)[6]	2100 cm⁻¹
t-C_4H_9	t-C_4H_9	—, 38	75–80°/58 (47.5–48.5°/10)[7]	2094 cm⁻¹
		—, 55[d]	120–125°/0.5	2132 cm⁻¹
		—, 45[e]	104–109°/0.2	2130 cm⁻¹

[a] Reacted at room temperature.

[b] Reacted at 0°.

[c] Contaminated with a small amount of an unknown product.

[d] $C_{15}H_{14}N_2$ (222.3) calc. C 81.05 H 6.35 N 12.60; found 81.07 6.39 12.52

[e] $C_{15}H_{20}N_2$ (228.3) calc. C 78.90 H 6.83 N 12.27; found 78.83 8.88 12.18

Preparation of Carbodiimides; General Procedure using Dilithiothioureas 1 (M = Li) and Sulfur Dioxide:

To a solution of a thiourea (15 mmol) in dry tetrahydrofuran (40 ml), butyllithium (33 mmol) in petroleum ether is added dropwise with stirring under dry nitrogen at room temperature. An excess of dry sulfur dioxide gas is slowly introduced to the solution under cooling with an ice-bath, then the inorganic salt 4 precipitates. After the mixture has been stirred for 30 min at room temperature, hexane (20 ml) is added to complete the precipitation of the salt 4 which is removed from the solution by centrifugal separation and is washed with hexane (10 ml). The combined hexane solution is distilled under vacuum to afford the carbodiimide 3.

General Procedure using Bis[bromomagnesio]thioureas 1 (M = MgBr) and Sulfur Dioxide:

To a solution of a thiourea (15 mmol) in dry tetrahydrofuran (10 ml), ethylmagnesium bromide (33 mmol) in tetrahydrofuran (40 ml) is added dropwise with stirring at room temperature. An excess of dry sulfur dioxide gas is introduced under cooling with an ice-bath, and the reaction mixture is stirred for 30 min at refluxing temperature. Hexane (30 ml) is added to precipitate the inorganic salt 4. After the salt 4 has been removed by decantation and is washed with hexane (10 ml), the solution is distilled under vacuum to give the carbodiimide 3.

The carbodiimides 3 isolated by distillation are identified by the comparisons of I.R. and N.M.R. spectra and b.p. with those of authentic samples.

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